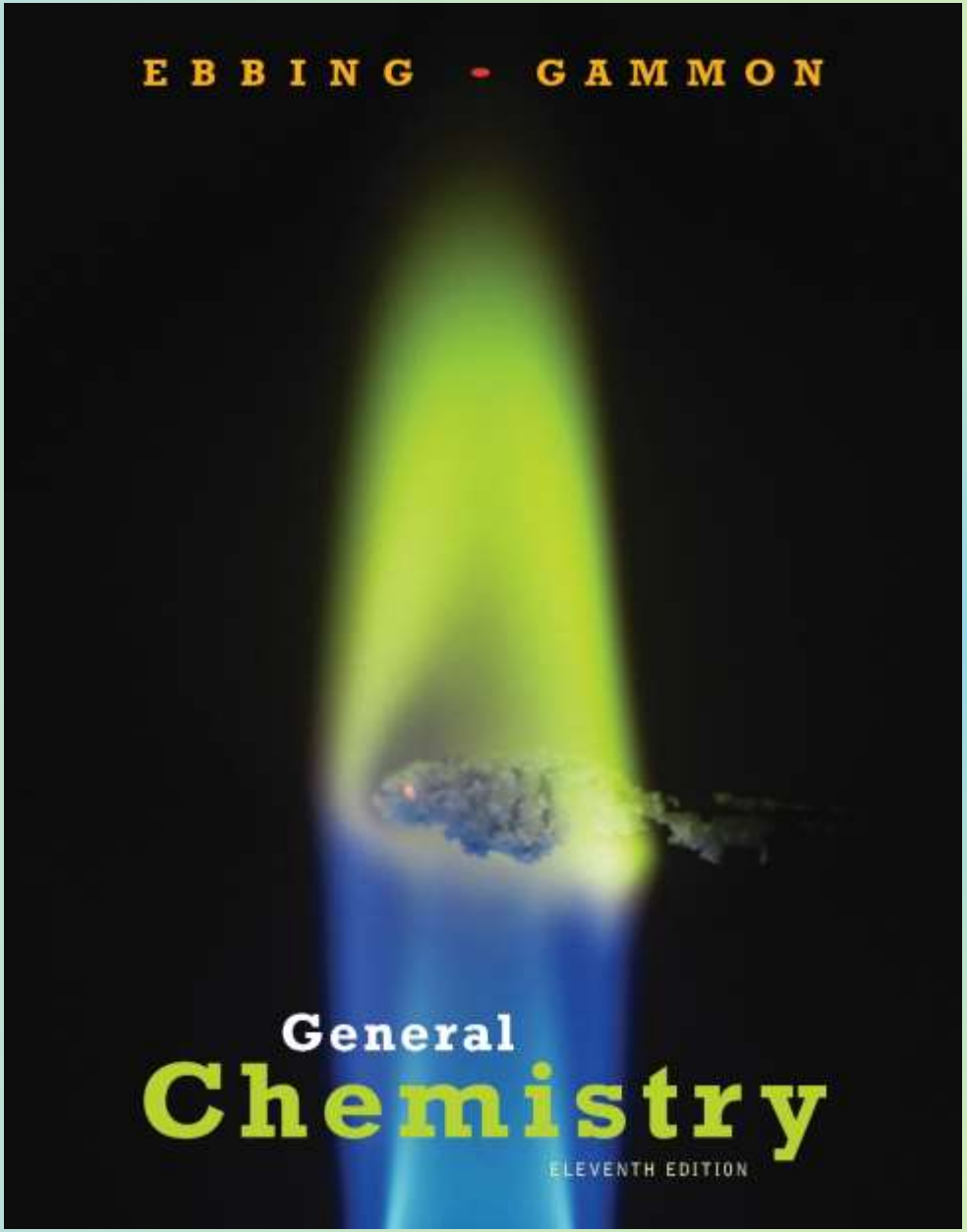

The Gaseous State

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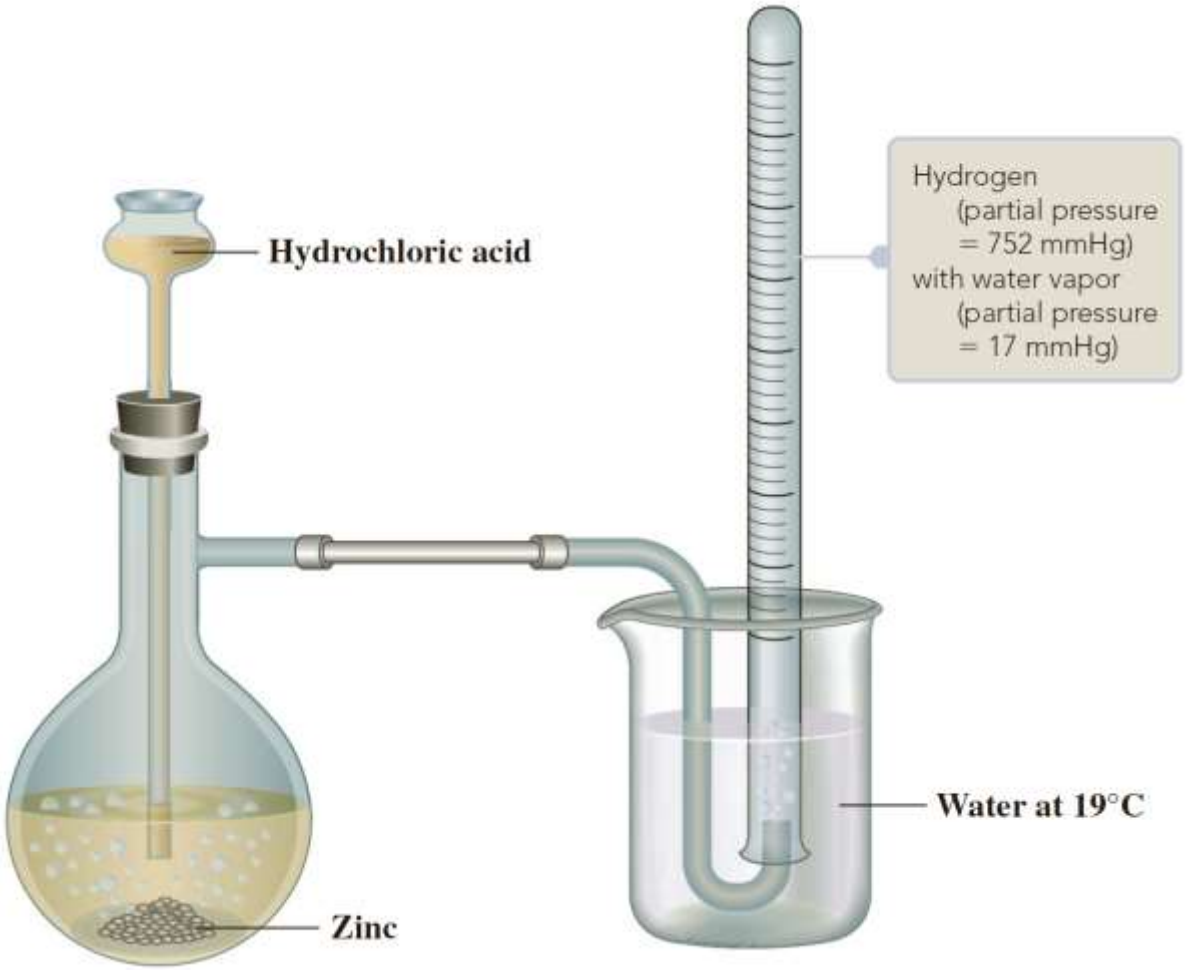
➢ Collecting Gases over Water



Vapor Pressure of Water at Various Temperatures*

Temperature (°C)	Pressure (mmHg)
0	4.6
10	9.2
15	12.8
17	14.5
19	16.5
21	18.7
23	21.1
25	23.8
27	26.7
30	31.8
40	55.3
60	149.4
80	355.1
100	760.0

Example 5.11

Hydrogen gas is produced according to the following reaction:

$$2HCl(aq) + Zn(s) \longrightarrow ZnCl_2(aq) + H_2(g)$$

The gas is collected over water. If 156 mL of gas is collected at 19°C and 769 mmHg total pressure, what is the mass of hydrogen collected? The vapor pressure of water at 19°C is 16.5 mmHg

(Q)An unknown gas was collected by water displacement. The following data was recorded: T = 27.0 °C; P = 750 torr;
V = 37.5 mL; Gas mass = 0.0873 g;
$P_{H_2O(vap)}$ = 26.98 torr
Determine the molecular weight of the gas.

A. 5.42 g/mol

B. 30.2 g/mol

C. 60.3 g/mol

D. 58.1 g/mol

E. 5.81 g/mol

➢ Kinetic-Molecular Theory

According to this theory, *a gas consists of molecules in constant random motion.*

Kinetic energy, E_k, is the energy associated with the motion of an object of mass *m.*

$$E_k = \tfrac{1}{2}m \times (\text{speed})^2$$

5.6 Kinetic Theory of an Ideal Gas

Kinetic-theory model of gas pressure According to kinetic theory, gas pressure is the result of the bombardment of the container walls by constantly moving molecules.

➢ Postulates of Kinetic Theory

Postulate 1: *Gases are composed of molecules whose size is negligible compared with the average distance between them.* Most of the volume occupied by a gas is empty space. This means that you can usually ignore the volume occupied by the molecules.

Postulate 2: *Molecules move randomly in straight lines in all directions and at various speeds.*
This means that properties of a gas that depend on the motion of molecules, such as pressure, will be the same in all directions.

Postulate 3: *The forces of attraction or repulsion between two molecules (intermolecular forces) in a gas are very weak or negligible, except when they collide.*
This means that a molecule will continue moving in a straight line with undiminished speed until it collides with another gas molecule or with the walls of the container.

Postulate 4: *When molecules collide with one another, the collisions are elastic.* In an elastic collision, the total kinetic energy remains constant; no kinetic energy is lost.

Postulate 5: *The average kinetic energy of a molecule is proportional to the absolute temperature*

➢ The Ideal Gas Law from Kinetic Theory

$$P \propto \text{frequency of collisions} \times \text{average force}$$

$$P \propto \left(u \times \frac{1}{V} \times N\right) \times mu$$

$$PV \propto Nmu^2$$

$$PV \propto nT$$

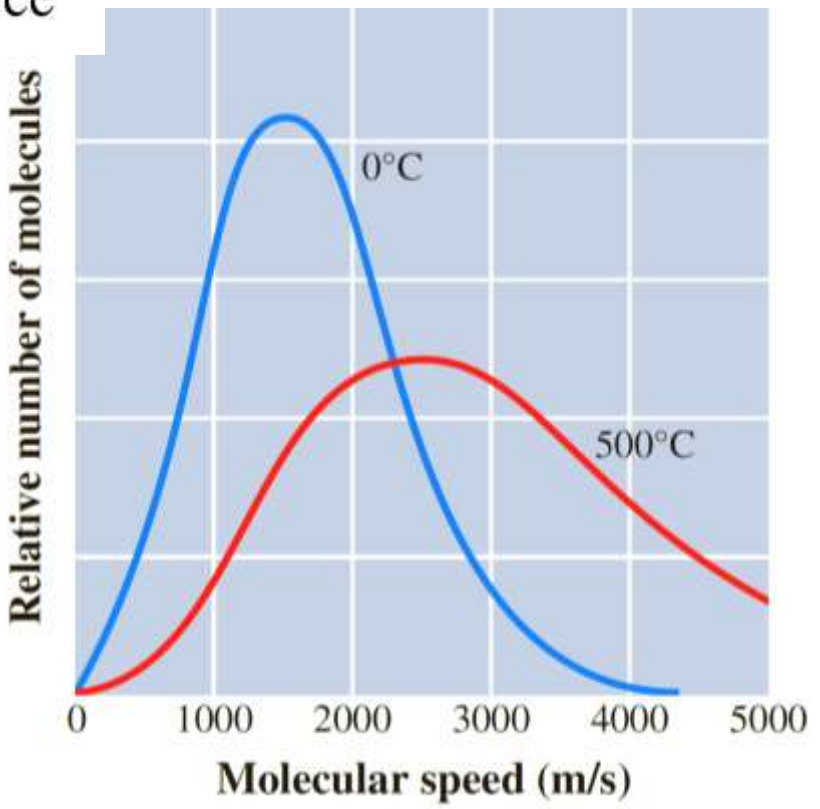
$$PV = nRT$$

5.7 Molecular Speeds; Diffusion and Effusion

➢ Molecular Speeds

root-mean-square (rms) molecular speed (*u*)

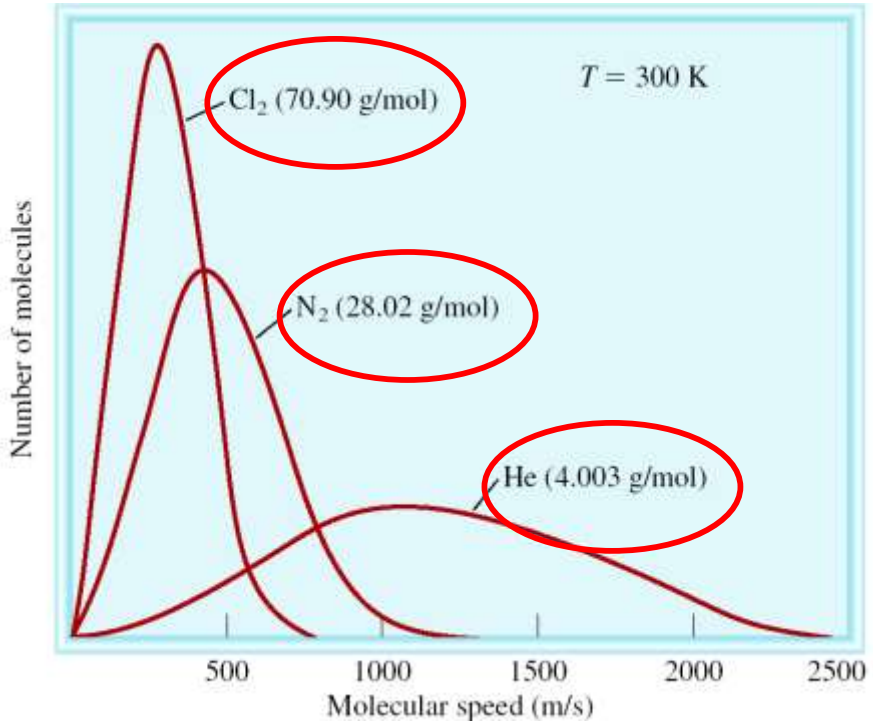
$$u = \sqrt{\frac{3RT}{M_m}} = \left(\frac{3RT}{M_m}\right)^{\frac{1}{2}}$$



Maxwell's distribution of molecular speeds The distributions of speeds of H_2 molecules are shown for 0°C and 500°C. Note that the speed corresponding to the maximum in the curve (the most probable speed) increases with temperature.

$$u = \sqrt{\frac{3RT}{M_m}} = \left(\frac{3RT}{M_m}\right)^{\frac{1}{2}}$$

R (= 8.314 kg·m^2/(s^2·K·mol)),
T (K), and M_m (kg/mol),



(Q) Calculate the rms speed of O_2 molecules in a cylinder at 21°C and 15.7 atm

$$u = \left(\frac{3 \times 8.31 \cancel{\text{kg}} \cdot \text{m}^2/(\text{s}^2 \cdot \cancel{\text{K}} \cdot \cancel{\text{mol}}) \times 294 \cancel{\text{K}}}{32.0 \times 10^{-3} \cancel{\text{kg}}/\cancel{\text{mol}}}\right)^{\frac{1}{2}} = \mathbf{479\ m/s}$$

Exercise 5.13 At what temperature do hydrogen molecules, H_2, have the same rms speed as nitrogen molecules, N_2, at 455°C? At what temperature do hydrogen molecules have the same average kinetic energy?

Determine the rms molecular speed for N_2 at 455°C (728 K):

$$u = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{3 \times 8.31\ \text{kg} \bullet \text{m}^2/(\text{s}^2 \bullet \text{K} \bullet \text{mol}) \times 728\ \text{K}}{28.02 \times 10^{-3}\ \text{kg/mol}}\right)^{\frac{1}{2}} = 804.81\ \text{m/s}$$

$$T = \frac{u^2 M}{3R} = \frac{(804.81\ \text{m/s})^2 (2.016 \times 10^{-3}\ \text{kg/mol})}{(3)(8.31\ \text{kg} \bullet \text{m}^2/\text{s}^2 \bullet \text{K} \bullet \text{mol})} = 52.4\ \text{K}$$

Any two gases at the same temperature will have the same average kinetic energy

Because the average kinetic energy of a molecule is proportional to only *T*

➢ Diffusion and Effusion

- ✓ **Diffusion** is *the process whereby a gas spreads out through another gas to occupy the space uniformly.*
- ✓ **Effusion** is *the process in which a gas flows through a small hole in a container*

- ✓ **Graham's law of effusion**

$$u = \sqrt{\frac{3RT}{M_m}}$$

Graham's law of effusion:

$$\text{Rate of effusion of molecules} \propto \frac{1}{\sqrt{M_m}}$$

(for the same container at constant T and P)

(Q) Calculate the ratio of effusion rates of molecules of carbon dioxide, CO_2, and sulfur dioxide, SO_2, from the same container and at the same temperature and pressure.

$$\frac{\text{Rate of effusion of } CO_2}{\text{Rate of effusion of } SO_2} = \frac{\frac{1}{\sqrt{M_m(CO_2)}}}{\frac{1}{\sqrt{M_m(SO_2)}}} \rightarrow$$

$$\frac{\text{Rate of effusion of } CO_2}{\text{Rate of effusion of } SO_2} = \sqrt{\frac{M_m(SO_2)}{M_m(CO_2)}} = \sqrt{\frac{64.1\ \text{g/mol}}{44.0\ \text{g/mol}}} = \mathbf{1.21}$$

carbon dioxide effuses 1.21 times faster than sulfur dioxide

Exercise 5.14 If it takes 3.52 s for 10.0 mL of He to effuse through a hole in a container at a particular temperature and pressure, how long would it take for 10.0 mL of O_2 to effuse from the same container at the same temperature and pressure? (Note that the **rate of effusion can be given in terms of volume of gas effused per second**.)

$$\frac{\text{Rate of effusion of } O_2}{\text{Rate of effusion of He}} = \sqrt{\frac{M_m(\text{He})}{M_m(O_2)}} = \sqrt{\frac{4.00 \text{ g/mol}}{32.00 \text{ g/mol}}} = 0.35$$

→ Rate of effusion of O_2 = 0.35 × rate of effusion of He.

$$\frac{\text{Volume of } O_2}{\text{Time for } O_2} = 0.35 \times \frac{\text{Volume of He}}{\text{Time for He}}$$

$$\frac{10.0 \text{ mL}}{\text{Time for } O_2} = 0.35 \times \frac{10.0 \text{ mL}}{3.52 \text{ s}}$$

$$\text{Time for } O_2 = \frac{3.52 \text{ s}}{0.35\underline{3}55} = 9.96 \text{ s}$$

Exercise 5.15 If it takes 4.67 times as long for a particular gas to effuse as it takes hydrogen under the same conditions, what is the molecular weight of the gas? (Note that the rate of effusion is inversely proportional to the time it takes for a gas to effuse.)

$$\frac{\text{Rate of effusion of } H_2}{\text{Rate of effusion of gas}} = \frac{\text{time for gas}}{\text{time for } H_2} = \sqrt{\frac{M_m(\text{gas})}{M_m(H_2)}} = 4.67$$

$M_m(\text{gas}) = (4.67)^2 \times M_m(H_2) = (4.67)^2 \times 2.016$ g/mol = 43.96g/mol

(Q) For the series of gases He, Ne, Ar, H_2, and O_2 what is the order of increasing rate of effusion?

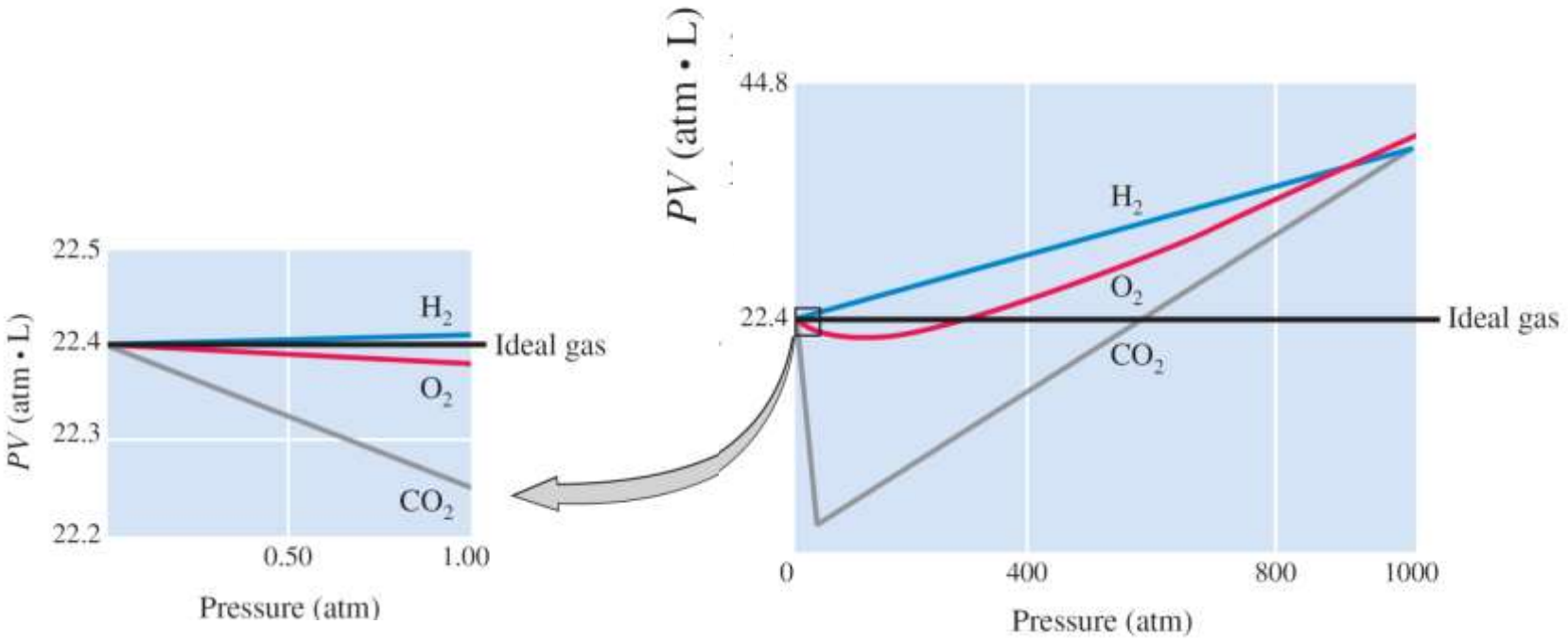
Substance	He	Ne	Ar	H_2	O_2
MM	4	20	40	2	32

Lightest are fastest: $H_2 > He > Ne > O_2 > Ar$

Same as: $Ar < O_2 < Ne < He < H_2$

5.8 Real Gases

Boyle's law (ideal gas) : PV = constant



Pressure–volume product of gases at different pressures

Right: The pressure–volume product of one mole of various gases at 0°C and at different pressures.

Left: Values at low pressure

The **van der Waals equation**
is *an equation similar to the ideal gas law, but includes two constants, a and b, to account for deviations from ideal behavior.*

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Ideal Gas Equation		***van der Waals Equation***
V	becomes	$V - nb$
P	becomes	$P + n^2a/V^2$

$$P(\text{actual}) = P(\text{ideal}) - n^2a/V^2$$

$$V(\text{actual}) = V(\text{ideal}) + nb$$

(Q)If sulfur dioxide were an ideal gas, the pressure at 0.0°C exerted by 1.000 mole occupying 22.41 L would be 1.000 atm (22.41 L is the molar volume of an ideal gas at STP). Use the van der Waals equation to estimate the pressure of this volume of 1.000 mol SO_2 at 0.0°C. See Table 5.7 for values of *a* and *b*.

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

Table 5.7 van der Waals Constants for Some Gases

Gas	*a* $L^2 \cdot atm/mol^2$	*b* L/mol
CO_2	3.658	0.04286
C_2H_6	5.570	0.06499
C_2H_5OH	12.56	0.08710
He	0.0346	0.0238
H_2	0.2453	0.02651
O_2	1.382	0.03186
SO_2	6.865	0.05679
H_2O	5.537	0.03049

$$P = \frac{1.000 \cancel{\text{mol}} \times 0.08206 \cancel{\text{L}}\cdot\text{atm}/(\cancel{\text{K}}\cdot\cancel{\text{mol}}) \times 273.2 \cancel{\text{K}}}{22.41 \cancel{\text{L}} - (1.000 \cancel{\text{mol}} \times 0.05679 \cancel{\text{L}}/\cancel{\text{mol}})} - \frac{(1.000 \cancel{\text{mol}})^2 \times 6.865 \cancel{\text{L}}^2\cdot\text{atm}/\cancel{\text{mol}}^2}{(22.41 \cancel{\text{L}})^2}$$

$$= 1.003 \text{ atm} - 0.014 \text{ atm} = \mathbf{0.989 \text{ atm}}$$